The Production of Automobile Emission Control Catalysts

GLOBAL CAPABILITY OF THE JOHNSON MATTHEY GROUP

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Stringent controls on automobile exhaust emissions are being introduced in the United States, Japan and most other industrialised countries. Catalysts based on the platinum group metals currently offer the best method of overcoming the problem. The Johnson Matthey Group, having developed suitable platinum-based catalytic reactor systems, is now constructing facilities to produce them.

Concern over aspects of environmental pollution caused by the internal combustion engine is now international and many governments have either adopted codes for control of exhaust emissions or are considering doing so. Photochemical smog is a phenomenon best known in California and in the area around Tokyo but the effects of uncontrolled emissions are serious before they reach such proportions where the hazard to health is obvious.

The principal pollutants present in automobile exhausts are carbon monoxide (CO), unburnt hydrocarbons (HC) and nitrogen oxides (NO_x). All are considered to be poisonous in various ways and current legislation is directed towards reducing their content to minimal levels in the exhaust gas stream finally released to the atmosphere from the engine burning gasoline. A full explanation of the problems involved in eliminating noxious emissions has been published previously in this journal (1).

The difficulties are exacerbated by the nature of the three principal pollutants. Whereas CO and HC can be oxidised to harmless carbon dioxide and water, given suitable conditions including the presence of sufficient oxygen, it is necessary to use the converse process of reduction to eliminate NO_x by converting it to inert nitrogen. Total elimination of the pollutant gases would be desirable but in practice this is unrealistic. In consequence the various pieces of legislation dealing with the matter specify maximum permitted levels of noxious emissions. As year succeeds year the values of these maxima are scheduled to decrease.

American Emission Standards

The Clean Air Amendments Act was passed in the United States in 1970. It laid down that there should be a 90 per cent reduction in CO and HC emissions from 1970 levels by 1975, and a 90 per cent reduction in NO_x emissions from 1971 model year levels by 1976.

U.S. Federal legislation in this field is enforced by the Environmental Protection Agency (E.P.A.). Hearings in Washington before members of E.P.A. were held in the early months of both 1972 and 1973. These were attended by the major automobile manufacturers and by the representatives of companies with devices to combat the exhaust pollution problem.

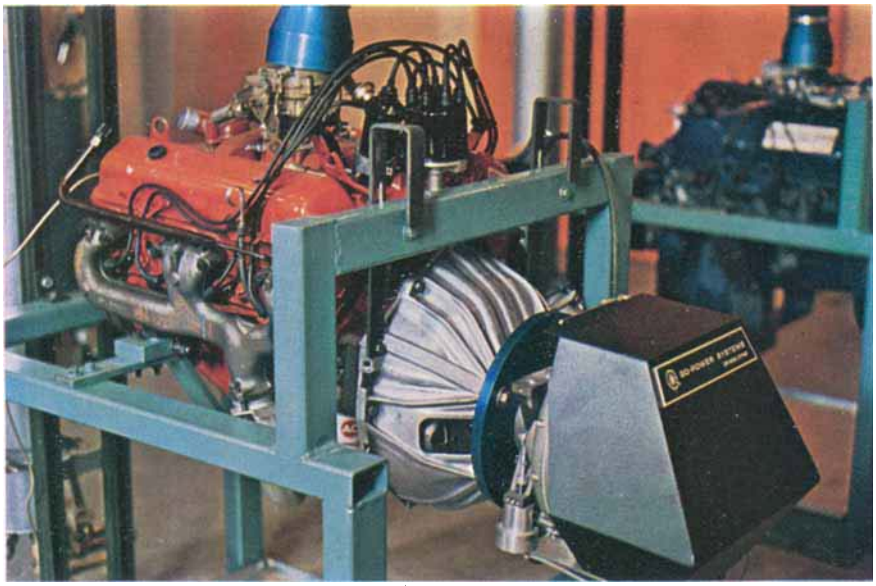
Johnson Matthey exhaust catalysts consist of elliptical or cylindrical ceramic honeycombs (left) which are treated with promoted platinum metals to produce units (right) for installation in emission control reactors. Size and shape depend on the space beneath the vehicle and on the engine capacity of that vehicle

Experience in the Johnson Matthey Group with platinum-based catalyst systems in many other applications, particularly in the abatement of other types of pollution – organic fumes and odours (2, 3), and nitric acid plant tail gas (4, 5) – had pointed to such catalysts as a suitable subject for investigation of the control of automobile exhaust emissions, and as a result of an intensive programme of laboratory investigations in England and the U.S.A. it was reported to E.P.A. in 1972 that catalyst systems developed by the Group could meet the original specifications laid down for 1975 and 1976 levels of automobile emissions in the United States. (See Table I). The principal E.P.A. test procedure is the constant volume sampling (CVS) test, which involves collection of the exhaust gases from engine start to engine stop over a simulated urban driving cycle

Table I
Trends in U.S. Federal Legislation Governing Automobile Emissions

	CO g/mile	HC g/mile	NO_x g/mile	Particulate g/mile	Evaporative g/test
1972*	39	3.4	—	—	2
1973	28	3.0	3.1	—	2
1975**	3.4	0.41	3.1	0.1	2
1976	3.4	0.41	0.4	0.03	2

*Introduction of CVS test **Introduction of revised CVS test



Research on exhaust emission characteristics has been carried out by the Johnson Matthey Group in both England and the United States, and a new testing sampling laboratory has been opened by Tanaka Matthey in Japan. Static engines are shown undergoing evaluation of catalyst performance at a Matthey Bishop test facility

lasting 23 minutes with the test vehicle on a roller dynamometer.

In addition to standard test procedures, a requirement of any emission control system is durability. U.S. regulations laid down that a system must be effective for 50,000 miles road use on a car. This has come to be interpreted as meaning, in the case of catalytic systems, that one catalyst replacement is permissible during that mileage, i.e. that a catalyst unit should last for 25,000 miles driving.

By 1972 the basic problems had been solved by Johnson Matthey Group engineers and scientists, and catalyst systems had been evolved with characteristics such as low ignition temperature, high thermal stability and good shock resistance. These catalyst systems consist of promoted platinum metals supported on honeycomb ceramic supports. There are two varieties; an oxidation-type catalyst is used to remove CO and HC from the exhaust gas stream and a reduction-type catalyst is used to deal with NO_x. In both cases the ceramic is shaped to fit into a stainless steel reactor approximating in size and shape to that of a conventional silencer (muffler).

Parameters were established by work with single cylinder engines. Testing then progressed to the point where systems were fitted to standard Chrysler and British Leyland vehicles on sale in the United Kingdom and to Ford vehicles on sale in the United States.

These tests established that the systems could meet the standards laid down by E.P.A. and that, providing automobile manufacturers decided early enough on their needs, it was feasible to construct production facilities within the E.P.A. time-scale.

Elsewhere many and varied attempts have been made to comply with E.P.A. regulations but during the past twelve months it has become clear that catalytic after-burners using platinum metals do offer the best chance for the next few years of satisfying the requirements of the U.S. authorities.

In April 1973 E.P.A. decided to modify its position on exhaust emission standards for the 1975 model year (see Table II). Interim standards were announced which, although not so rigorous as those previously published,

Matthey Bishop test facilities incorporate equipment for control of dynamometers and for exhaust emission analysis while monitoring automobile engines performing simulated driving cycles. Evaluation of catalyst performance is the basis of work to improve catalysts

are nevertheless severe, since they will lead to a big reduction of automobile exhaust pollution from 1973 levels. The interim regulations for California are more severe than for the rest of the United States because of the seriousness of the problem there. California is a large state with a very high number of new vehicle registrations each year. Therefore the stricter interim standards for California will have a considerable effect on the plans of automobile manufacturers.

Table II
Maximum Permitted Emissions for 1975 Model Year Vehicles

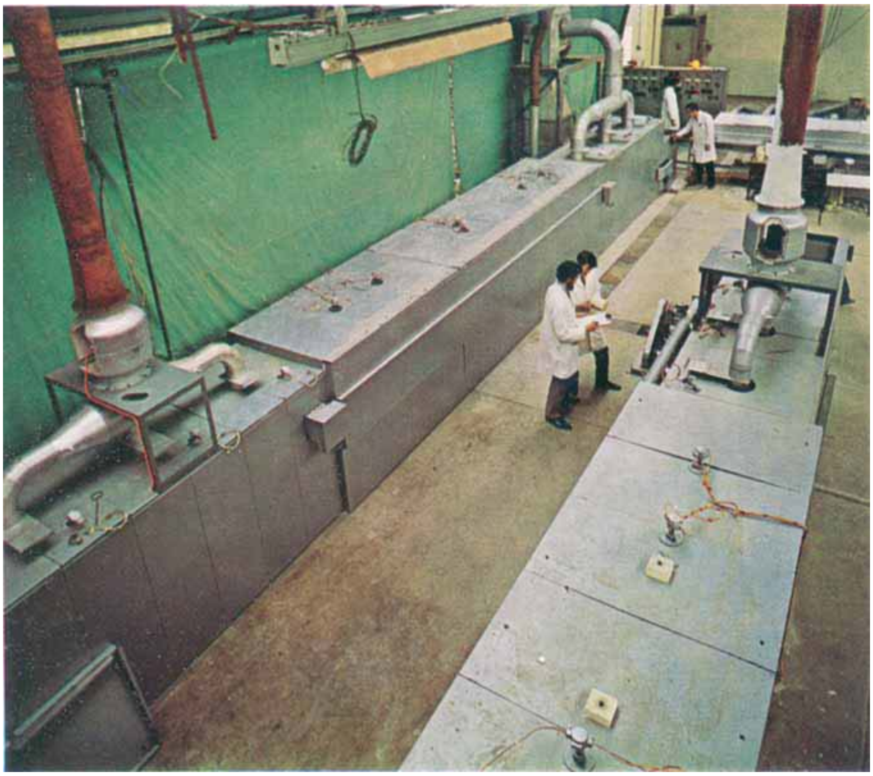
	CO g/mile	HC g/mile	NO_x g/mile
1973 level	28.0	3.0	3.1
1975 level proposed originally by E.P.A.	3.4	0.41	3.1
1975 interim level for California	9.0	0.9	2.1
1975 interim level for rest of U.S.A.	15.0	1.5	3.1

The three major American car companies have announced that they do not propose to contest these latest E.P.A. findings and proposals and will fit catalytic converters to all 1975 model year cars sold in California and to some sold in other states.

Japanese Emission Standards

The Japanese Government has acted separately to curb automobile exhaust pollution. It has announced standards to be applied to new models from 1st April 1973 and to new vehicles of existing models from 1st December 1973. Gasoline-engined vehicles under 2.5 tonnes in weight must limit their exhaust emissions to 18.4 g of CO, 2.94 g of HC and 2.18 g of NO_x per kilometre. These are, however, interim measures. Standards to be introduced in 1975 and 1976 will be comparable to or even stricter than those of the United States. The Japanese Government is also insisting that catalytic after-burners must be installed on all cars with engines of 1800 cc capacity or more that are in use on 1st April 1973.

Both for their domestic market and for export, Japanese automobile manufacturers



Full-scale production of catalyst units for the control of automobile exhaust emissions is planned to take place at Matthey Bishop's Devon, Pennsylvania facility and at the plant shown here of Johnson Matthey Chemicals Limited at Royston, England

are evaluating platinum exhaust catalysts. Large numbers of Japanese cars are exported to America and their emissions must meet E.P.A. standards. However, the Japanese standards are being introduced to improve the quality of life in Japan and not merely for reasons of international trade.

Other Standards

Many other nations are still working on programmes of standards to control automobile exhaust emissions. Canada is expected to introduce regulations similar to those of the United States. Countries in Europe are considering the problem – obviously a uniform standard for Europe would be desirable.

All automobile manufacturers in countries where standards have not yet been adopted must, however, conform to existing regulations in those countries to which they wish to export. This greatly affects European cars exported to America.

World-wide Production Facilities

The programme of work within the Johnson Matthey Group has broadened in the last year. Having shown the feasibility of their system, research and development teams have been striving to optimise its features. All components of the system have been under test, with special emphasis on ensuring that each catalyst unit possesses adequate durability. Potential limitations to catalyst life have been identified and their causes have been minimised or eliminated.

Such work has led to a considerable expansion of basic and development testing, and the engine and vehicle testing areas of the English and American laboratories have been extended. A new testing and sampling laboratory has also now been opened by Tanaka Matthey in Japan.

Plans for mass production of catalyst units have proceeded simultaneously with the testing programme. Following the development of a successful pilot plant, two full-scale production plants are being built, one at Johnson Matthey Chemicals factory at Royston, England and the other at Matthey Bishop's Devon, Pennsylvania facility.

The difficulties of eliminating the hazards caused by automobile exhaust emissions have posed formidable problems. Of the alternative systems for the control of these emissions, platinum catalysts offer the best prospect of solving difficulties at the present time.

Doubts about the availability of platinum to equip all the new vehicles that will have to conform with the more stringent emission standards – engendered in part by the campaign to secure postponement of the legislation – are no longer realistic. What might at one time have been regarded as a difficult supply situation in the first year is no longer likely. The slower introduction of the more stringent standards provides time for the expansion programme already undertaken at Rustenburg to become effective before the full requirements are felt. In addition, as has so often been the case when a new major use of platinum is introduced, development of the technology has shown that less platinum will be needed in each device than had earlier been contemplated. At this time it seems clear that sufficient platinum will be available to satisfy the growth requirements of the established users and to provide comfortably for the needs of the automobile industry.

References

1 G. J. K. Acres and B. J. Cooper, *Platinum Metals Rev.*, 1972, **16**, (3), 74–86
2 G. J. K. Acres, *Platinum Metals Rev.*, 1970, **14**, (1), 2–10; *Ibid.*, 1971, **15**, (1), 9–12; *Ibid.*, (4), 132–133
3 G. J. K. Acres, *Platinum Metals Rev.*, 1970, **14**, (3), 78–85
4 J. B. Hunter, *Platinum Metals Rev.*, 1968, **12**, (1), 2–6
5 R. A. Searles, *Platinum Metals Rev.*, 1973, **17**, (2), 57–63

Rhodium and Iridium of Improved Ductility

Rhodium and iridium are more difficult to work than any other face-centred cubic metal and no completely satisfying explanation for this anomalous behaviour has yet been advanced. It is now ten years since Dr Reinacher of Degussa first demonstrated the advantages of platinum sheathing, which allowed working temperatures to be reduced to levels which encouraged the formation of a fibrous texture within the wire or sheet being produced.

Platinum, however, tends to alloy with the rhodium or iridium being worked and is very difficult to remove completely by etching, so cheaper and more effective alternatives have been sought. Dr Reinacher has now shown (*Metall*, 1973, **27**, (1), 1–4) that rhodium and iridium of excellent ductility can be obtained by working within a pure nickel envelope which can be readily removed by etching.

Hot rolled rhodium and iridium rods having a diameter of about 3 mm were sealed within nickel tubes having a wall thickness of 1.8 mm. The rhodium assemblies were then rolled at temperatures of 800°C and below into wires approximately 1 mm diameter. The iridium assemblies needed working at 1000°C to avoid cracking on rolling.

Rhodium wires with a fibrous structure and high ductility were then obtained by etching away the nickel sheath and drawing the wire through carbide dies at temperatures down to 350°C. Higher temperatures were needed for drawing the iridium wires and, since sheath removal was found to be essential for the production of round wire of uniform diameter, complete freedom from cracking was only avoided by working at 1000°C. Iridium wire so produced retained its fibrous structure and at a diameter of 0.2 mm could be safely coiled round a 2 mm mandrel.

The effectiveness of this procedure is attributed by Dr Reinacher to the way the nickel isolates the surface of the refractory noble metal from the severe local and unsymmetrical deformations inevitably associated with hot working in grooved rolls.